

=> d 16 cit fd

1. 5,538,942, Jul. 23, 1996, Method for producing a superconducting magnet coil; Toru Koyama, et al., 505/430; 174/125.1; 335/216; 427/62, 116, 177; 428/457, 930; 505/705, 813, 884, 887 [IMAGE AVAILABLE]

US PAT NO: 5,538,942 [IMAGE AVAILABLE] L6: 1 of 13

DATE FILED: Jan. 20, 1995

=> d 16 2- cit fd

2. 5,384,197, Jan. 24, 1995, Superconducting magnet coil and curable resin composition used therein; Toru Koyama, et al., 428/457; 174/125.1; 335/216; 428/458, 473.5, 474.4, 930; 505/705, 813, 884, 887 [IMAGE AVAILABLE]

US PAT NO: 5,384,197 [IMAGE AVAILABLE] L6: 2 of 13

DATE FILED: Dec. 22, 1993

3. 5,364,917, Nov. 15, 1994, Perfluorocyclobutane ring-containing polymers; David A. Babb, et al., 526/242; 264/328.1, 331.11, 331.19, 331.21; 526/243, 244, 245, 247, 248, 250, 251, 252, 253, 255; 528/86 [IMAGE AVAILABLE]

US PAT NO: 5,364,917 [IMAGE AVAILABLE] L6: 3 of 13

DATE FILED: Dec. 1, 1993

4. 5,178,675, Jan. 12, 1993, Alkoxy silane adhesive compositions; Fred H. Sexsmith, 106/287.11, 13, 15.05, 16; 528/38 [IMAGE AVAILABLE]

US PAT NO: 5,178,675 [IMAGE AVAILABLE] L6: 4 of 13

DATE FILED: Mar. 22, 1991

5. 5,173,544, Dec. 22, 1992, \*\*Epoxy\*\* resin compositions; Hisashi Shimizu, et al., 525/476; 523/433, 435; 525/487, 524; 528/27 [IMAGE AVAILABLE]

US PAT NO: 5,173,544 [IMAGE AVAILABLE] L6: 5 of 13

DATE FILED: May 16, 1990

6. 5,159,038, Oct. 27, 1992, Perfluorocyclobutane ring-containing polymers; David A. Babb, et al., 526/242, 243, 244, 245, 246, 247, 252, 255 [IMAGE AVAILABLE]

US PAT NO: 5,159,038 [IMAGE AVAILABLE] L6: 6 of 13

DATE FILED: Mar. 22, 1991

7. 5,037,917, Aug. 6, 1991, Perfluorocyclobutane ring-containing polymers; David A. Babb, et al., 526/242, 243, 245, 247, 248, 250, 251, 252, 253, 255; 528/86; 568/669 [IMAGE AVAILABLE]

US PAT NO: 5,037,917 [IMAGE AVAILABLE] L6: 7 of 13  
DATE FILED: Jun. 9, 1989

8. 4,940,740, Jul. 10, 1990, Single phase toughened heat-curable resin systems exhibiting high strength after impact; Thomas Folda, et al., 523/428, 468; 525/524; 528/103 [IMAGE AVAILABLE]

US PAT NO: 4,940,740 [IMAGE AVAILABLE] L6: 8 of 13  
DATE FILED: Apr. 21, 1989

9. 4,891,417, Jan. 2, 1990, \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers; Alberto Re, et al., 528/112, 402 [IMAGE AVAILABLE]

US PAT NO: 4,891,417 [IMAGE AVAILABLE] L6: 9 of 13  
DATE FILED: Mar. 10, 1989

10. 4,833,227, May 23, 1989, \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers; Alberto Re, et al., 528/73, 103, 104, 108, 110, 401, 402 [IMAGE AVAILABLE]

US PAT NO: 4,833,227 [IMAGE AVAILABLE] L6: 10 of 13  
DATE FILED: Dec. 10, 1987

11. 4,699,969, Oct. 13, 1987, Fluorinated polymers and resins prepared therefrom; Alberto Re, et al., 528/70; 427/130, 131, 132; 428/413, 418, 423.3, 694BF, 694BP, 694TF, 900; 528/110, 401, 402 [IMAGE AVAILABLE]

US PAT NO: 4,699,969 [IMAGE AVAILABLE] L6: 11 of 13  
DATE FILED: Jul. 22, 1986

12. 4,413,094, Nov. 1, 1983, Perfluoroelastomer blends; Carl A. Aufdermarsh, Jr., 525/187; 433/200.1; 525/186, 200 [IMAGE AVAILABLE]

US PAT NO: 4,413,094 [IMAGE AVAILABLE] L6: 12 of 13  
DATE FILED: Sep. 29, 1982

13. 4,339,565, Jul. 13, 1982, Adhesive composition for fluorinated rubbers; Masayasu Tomoda, 528/27; 106/287.11, 287.12, 287.13, 287.14, 287.15, 287.16 [IMAGE AVAILABLE]

US PAT NO: 4,339,565 [IMAGE AVAILABLE] L6: 13 of 13  
DATE FILED: Nov. 28, 1980

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L7

7 L6 AND CURING AGENT

=> d 17 1-

1. 5,538,942, Jul. 23, 1996, Method for producing a superconducting magnet coil; Toru Koyama, et al., 505/430; 174/125.1; 335/216; 427/62, 116, 177; 428/457, 930; 505/705, 813, 884, 887 [IMAGE AVAILABLE]
2. 5,384,197, Jan. 24, 1995, Superconducting magnet coil and curable resin composition used therein; Toru Koyama, et al., 428/457; 174/125.1; 335/216; 428/458, 473.5, 474.4, 930; 505/705, 813, 884, 887 [IMAGE AVAILABLE]
3. 5,173,544, Dec. 22, 1992, \*\*Epoxy\*\* resin compositions; Hisashi Shimizu, et al., 525/476; 523/433, 435; 525/487, 524; 528/27 [IMAGE AVAILABLE]
4. 4,940,740, Jul. 10, 1990, Single phase toughened heat-curable resin systems exhibiting high strength after impact; Thomas Folda, et al., 523/428, 468; 525/524; 528/103 [IMAGE AVAILABLE]
5. 4,891,417, Jan. 2, 1990, \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers; Alberto Re, et al., 528/112, 402 [IMAGE AVAILABLE]
6. 4,833,227, May 23, 1989, \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers; Alberto Re, et al., 528/73, 103, 104, 108, 110, 401, 402 [IMAGE AVAILABLE]
7. 4,339,565, Jul. 13, 1982, Adhesive composition for fluorinated rubbers; Masayasu Tomoda, 528/27; 106/287.11, 287.12, 287.13, 287.14, 287.15, 287.16 [IMAGE AVAILABLE]

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US PAT NO: 4,940,740 [IMAGE AVAILABLE]

L7: 4 of 7

ABSTRACT:

Heat curable \*\*epoxy\*\* resin systems are disclosed which may be cured to form monophasic matrix resins and adhesives which, when utilized as matrix. . .

SUMMARY:

BSUM(3)

The subject invention relates to heat-curable \*\*epoxy\*\* resin systems having exceptional resistance to impact induced damage. More particularly, the subject invention relates to toughened \*\*epoxy\*\* resin

systems which when cured are monophasic and which are capable of preparing carbon reinforced composites having compression after impact.

SUMMARY:

BSUM(5)

\*\*Epoxy\*\* resins have been widely used in the field of structural materials as matrix resins for fiber reinforced prepgres and as structural adhesives. However, it is difficult to achieve both high strength and toughness in \*\*epoxy\*\* systems, even when cured with curing agents such as the diaminodiphenylsulfones. When used as prepregging resins with carbon fibers, for. . .

SUMMARY:

BSUM(6)

In the past, high CAI values have required resort to multiphase systems. For example, in EP-A-0 252 725, \*\*epoxy\*\* resins are combined with \*\*epoxy\*\* or amine functional polyarylene ether sulfone oligomers, \*\*epoxy\*\* curing agents, and from 1 to about 16 percent of an infusible elastomer having a particle size of from 10 to about 75 .mu.m. In addition to the discontinuous phase created by the infusible rubber particles, the cured \*\*epoxy\*\* system itself is multiphasic, having a discontinuous glassy \*\*epoxy\*\* phase dispersed in a continuous glassy polysulfone thermoplastic rich phase.

SUMMARY:

BSUM(11)

It has now been discovered that heat-curable \*\*epoxy\*\* resin systems may be formulated which exhibit but a single phase upon cure, and which are capable of preparing carbon/graphite. . . and in particular greater than 43 ksi after an impact of 1500 in-lb/in. Such resin systems are formulated with an \*\*epoxy\*\* resin component having a functionality of two or greater, an aromatic diamine \*\*curing\*\* \*\*agent\*\*, and an \*\*epoxy\*\* resin/diphenol prereact of limited \*\*molecular\*\* \*\*weight\*\*. Such resin systems also possess excellent out-time, and are suitable as matrix resins for fiber-reinforced composites and as structural adhesives.

SUMMARY:

BSUM(13)

The \*\*epoxy\*\* resins useful as the \*\*epoxy\*\* resin component in the practice of the subject invention are well known to those skilled in the art. Such \*\*epoxy\*\* resins have functionalities of two or greater, preferably two through four, and are generally prepared by the condensation of epichlorohydrin with an active hydrogen compound in the presence of base. The methods of \*\*epoxy\*\* resin synthesis as well as the physical characteristics of many \*\*epoxy\*\* resins may be found in the treatise Handbook of \*\*Epoxy\*\* Resins, Lee & Neville, Ed.s., McGraw-Hill, New York, .COPYRGT.1967.

SUMMARY:

BSUM(14)

Particularly suitable \*\*epoxy\*\* resins are the so-called DGEBF \*\*epoxy\*\* resins and the glycidyl derivatives of the dihydroxynaphthalenes; the phenol terminated dicyclopentadiene and dicyclopentadiene oligomers as taught by U.S. Pat.. . .

SUMMARY:

BSUM(16)

\*\*Epoxy\*\* resins which are useful in preparing the \*\*epoxy\*\*-phenol prereacts of the present invention generally have functionalities of about 2, i.e. preferably from about 1.8 to about 2.2. Suitable. . . epoxies have been listed previously, and additional epoxies may be found in the Lee & Neville treatise and the treatise \*\*Epoxy\*\* Resins Chemistry and Technology, Marcel Dekker, Inc., New York, May and Tanaka, Ed.s., .COPYRGT.1973.

SUMMARY:

BSUM(17)

Diphenols . . . having an average of two phenolic hydroxyls per molecule. Particularly well suited, for example, are the bisphenols, particularly bisphenol A, \*\*bisphenol\*\* \*\*AF\*\*, bisphenol F, bisphenol O, bisphenol S, bisphenol P, bisphenol M, bisphenol AP, 3,4'-bisphenol A, 4,4'-dihydroxybiphenyl and the substituted bisphenols, especially. . .

SUMMARY:

BSUM(19)

The preferred prereacts of the subject invention are prepared by

reacting a stoichiometric excess of a substantially difunctional \*\*epoxy\*\* resin with a diphenol until all the phenolic hydroxyl groups have reacted. The reaction takes place either neat or in. . . C. and most preferably from about 135.degree. C. to about 150.degree. C. A catalyst which promotes the reaction of the \*\*epoxy\*\* group with phenolic hydroxyl groups is generally required, except perhaps in the case of the dihydroxynaphthalenes which have been found. . .

SUMMARY:

BSUM(20)

Suitable catalysts for the \*\*epoxy\*\*-phenol addition reaction are well known to those skilled in the art. Strong bases such as sodium or potassium hydroxide may. . .

SUMMARY:

BSUM(22)

The . . . reactions are carried out to completion, as the presence of small quantities of phenols may catalyze the reaction between the \*\*epoxy\*\* group and the amino group of the \*\*curing\*\* \*\*agent\*\*. When this occurs, the out-time of the resin is undesirably short, and is a major reason why polyphenols have not. . . high performance amine curing agents such as 4,4'-diaminodiphenylsulfone. The reaction progress may be monitored by observing the decrease in the \*\*epoxy\*\* equivalent weight of the mixture, observing the change in viscosity, or the disappearance of phenolic hydroxy groups.

SUMMARY:

BSUM(23)

By . . . the final resin composition which contains all the necessary components and additives including any catalysts. The necessary components are the \*\*epoxy\*\* resin component, the prereact component, and the \*\*curing\*\* \*\*agent\*\*. Optional additives include auxiliaries such as fillers, plasticizers, pigments, rheology control agents and the like. Thermoplastic and other tougheners may. . .

SUMMARY:

BSUM(24)

The \*\*molecular\*\* \*\*weight\*\* of the prereact component should be low enough so as to avoid phase separation upon curing of the heat-curable

resin system. In general, the \*\*molecular\*\* \*\*weight\*\* of the prereact should be less than 5000 Daltons, preferably less than 2000 Daltons, and more preferably less than 1000 Daltons. However, these \*\*molecular\*\* \*\*weight\*\* limitations are system dependent, particularly with regard to the nature of the prereact components and the \*\*epoxy\*\* resin components. Thus a simple test for compatibility is the most practical manner of assessing whether a particular prereact is. . . and visually observing the clarity of the casting. If the casting is turbid, then phase separation has occurred and the \*\*molecular\*\* \*\*weight\*\* of the prereact is not suitable for that particular resin system.

SUMMARY:

BSUM(25)

The heat-curable resin systems of the subject invention generally contain from 10 to about 80 percent of the \*\*epoxy\*\* resin component, from 10 to about 50 percent by weight of the prereact component, and an amount of \*\*curing\*\* \*\*agent\*\* ranging from 0.8 to about 1.6 times the stoichiometric amount calculated from the \*\*epoxy\*\* equivalent weights of the \*\*epoxy\*\* resin component and the prereact component. The resin system may also contain from 0.001 to about 5.0 weight percent of. . . one is required. The foregoing percentages are based on the total weights of the resin system components, that is, the \*\*epoxy\*\* resin(s), the prereact(s), the \*\*curing\*\* \*\*agent\*\*(s) and the catalyst(s). In addition to these resin system components, the final heatcurable resin system may contain up to 30. . .

SUMMARY:

BSUM(30)

It . . . tacky and moreover, be able to maintain this tack over extended periods, particularly at room temperature conditions. Resin systems containing \*\*epoxy\*\* resins, phenols, and amine-functional curing agents cannot meet this requirement; Example 9 is illustrative of the effect of this loss. . .

DETDESC:

DETD(3)

To 1000 grams of an \*\*epoxy\*\* resin having a functionality of 2.2 and an \*\*epoxy\*\* equivalent weight of approximately 230, and which may be prepared through the reaction of epichlorohydrin with phenolated dicyclopentadiene as disclosed. . . excursion to 163.degree. C. The mixture was stirred for one hour at 150.degree. C., yielding a prereact

with a theoretical \*\*molecular\*\* \*\*weight\*\* of 1070. To the prereact was then added 1000 g of a DGEBF \*\*epoxy\*\* resin having an \*\*epoxy\*\* equivalent weight of 165. After cooling to 90.degree. C., 741 g of 4,4'-diaminodiphenylsulfone was added. Tg of the resulting heat-curable.

DETDESC:

DETD(7)

To 500 g of DGEBF \*\*epoxy\*\* resin having an \*\*epoxy\*\* equivalent weight of 165 was added 200 g 2,7-dihydroxynaphthalene. The mixture was heated to 150.degree. C. in the absence of. . .

DETDESC:

DETD(9)

To 700 g DGEDCPD \*\*epoxy\*\* was added 200 g 1,5-dihydroxynaphthalene. The mixture was heated, and 0.5 g ethyltriphenylphosphonium iodide added when the temperature reached 107.degree.. . . mixture reached 135.degree. C., it was stirred for two hours at that temperature following which 488 g of a DGEBF \*\*epoxy\*\* having an \*\*epoxy\*\* equivalent weight of 165 was added. After stirring for one hour more, an additional 812 g of DGEBF \*\*epoxy\*\* was added, and the mixture cooled to 90.degree. C. whereupon 755 g 4,4'-diaminodiphenylsulfone was added. A neat sample of this. . .

DETDESC:

DETD(13)

To 700 g DGEDCPD \*\*epoxy\*\* at 90.degree. C. was added 600 g tetrabromobisphenol A and 0.5 g ethyltriphenylphosphonium iodide. The mixture was stirred at 150.degree. C. for four hours. While the viscosity was rapidly increasing, 400 g of DGEBF \*\*epoxy\*\* having an \*\*epoxy\*\* equivalent weight of 165 was added. When the reaction was complete, as evidenced by no further change in viscosity, it was cooled to 121.degree. C. whereupon 800 g of DGEBF \*\*epoxy\*\* which had been preheated to 120.degree. C. was added. At 90.degree. C., 728 g 4,4'-diaminodiphenylsulfone was added. Although the out. . .

DETDESC:

DETD(15)

An experimental resin system, believed to contain an \*\*epoxy\*\* resin, a phenol-functional \*\*curing\*\* \*\*agent\*\*, and a blocked catalyst, available

from Dow Chemical Co., Midland, Mich. and designated XU71794.00, was heated to 150.degree. C. without addition of other ingredients. While the viscosity was rapidly increasing, 200 g of a DGEBF \*\*epoxy\*\* resin having an \*\*epoxy\*\* equivalent weight of 165 was added. Stirring was continued for four hours at 150.degree. C. following which an additional 800 g DGEBF \*\*epoxy\*\* resin was added, the mixture cooled to 90.degree. C., and 582 g 4,4'-diaminodiphenylsulfone added. The heat-curable resin system had tack. . .

DETDESC:

DETD(17)

Eight . . . by which time the viscosity had risen so high that effective stirring was no longer possible, indicating that a high \*\*molecular\*\* \*\*weight\*\* prereact had been obtained. At this point, 185 g of DGEBF was added, the mixture cooled to 90.degree. C., and. . .

DETDESC:

DETD(21)

To 1000 g of the DGEDCPD \*\*epoxy\*\* described in Example 1 was added 198 g of 4,4'-dihydroxybiphenyl at 165.degree. C. The mix was cooled to 150.degree. C.. . . 198.degree. C. following which the temperature was reduced to 150.degree. C. After mixing for 30 minutes, 1000 g of DGEBF \*\*epoxy\*\* was added, the mixture was cooled to 90.degree. C., and 741 g of 4,4'-diaminodiphenylsulfone added. A cured casting of this. . .

DETDESC:

DETD(23)

To 1000 grams of a bisphenol F derived \*\*epoxy\*\* resin having an \*\*epoxy\*\* equivalent weight of 165 was added 1170 grams of a prereact which may be prepared from a bisphenol A based \*\*epoxy\*\* resin having a functionality of two and a low \*\*epoxy\*\* equivalent weight and bisphenol A. The prereact is commercially available from the DOW Chemical Co., as D.E.R. 661 \*\*epoxy\*\* resin having an \*\*epoxy\*\* equivalent weight of about 525. The \*\*curing\*\* \*\*agent\*\*, 745 grams of 4,4'-diaminodiphenylsulfone, was added at 160.degree. F. along with 5 grams of borontrifluoride monoethylamine catalyst. No phase separation. . .

DETDESC:

DETD(25)

To 170 grams of 2,7-dihydroxynaphthalene was added 1000 grams of an experimental \*\*epoxy\*\* resin mixture available from DOW as XP71756.01. After heating until complete dissolution, 1.5 grams ethyltriphenylphosphonium iodide was added and the mixture processed as before. To this prereact was added 1000 grams of a bisphenol F based \*\*epoxy\*\* resin having an \*\*epoxy\*\* equivalent weight of 165. 741 grams of 4,4'-diaminodiphenylsulfone \*\*curing\*\* \*\*agent\*\* was added at 160.degree. F. Castings remained clear indicating no phase separation.

CLAIMS:

CLMS (1)

The . . . are defined as follows:

1. A heat-curable resin system, comprising:

(a) from 10 to about 80 weight percent of an \*\*epoxy\*\* resin component;  
(b) from 10 to about 50 weight percent of a prereact component; and  
(c) from 0.8 to about 1.6 equivalents, based upon the \*\*epoxy\*\* groups in components (a) and (b), of an aromatic diamine \*\*curing\*\* \*\*agent\*\*;  
wherein said prereact component (b) is the essentially phenolic hydroxyl-free reaction product of an \*\*epoxy\*\* resin and a diphenol;  
wherein the \*\*molecular\*\* \*\*weight\*\* of component (b) is such that phase separation does not result upon cure of the heat-curable resin system;  
and wherein. . . .

CLAIMS:

CLMS (4)

4. The composition of claim 1 wherein said prereact component (b) is prepared through the reaction of an \*\*epoxy\*\* resin with a diphenol selected from the group consisting of the bisphenols; resorcinol; hydroquinone; the dihydroxynaphthalenes; the dihydroxybiphenyls; the phenolated. . . .

CLAIMS:

CLMS (5)

5. The composition of claim 1 wherein said \*\*epoxy\*\* resin in prereact component (b) is a glycidyl derivative of a diphenol selected from the group consisting of bisphenol A,. . . .

CLAIMS:

CLMS (6)

• 6. The composition of claim 1 wherein the \*\*epoxy\*\* resin component (a) is a glycidyl derivative of a diphenol selected from the group consisting of bisphenol A; bisphenol F; . . .

CLAIMS:

CLMS (7)

7. The composition of claim 1 wherein said \*\*curing\*\* \*\*agent\*\* (c) is selected from the group consisting of the diaminodiphenylmethanes; 2,2-bis[diaminophenyl]propanes; diaminobenzenes; diaminodiphenyloxides; diaminophenylsulfides; diaminodiphenylsulfones; and the aminophenyl terminated polyarylene. . .

CLAIMS:

CLMS (8)

8. The composition of claim 4 wherein said \*\*epoxy\*\* resin in component (b) is a glycidyl derivative of a diphenol selected from the group consisting of bisphenol A; bisphenol. . .

CLAIMS:

CLMS (9)

9. The composition of claim 6 wherein said \*\*epoxy\*\* resin in component (b) is a glycidyl derivative of a diphenol selected from the group consisting of bisphenol A; bisphenol. . .

CLAIMS:

CLMS (17)

17. . . heat curable prepreg comprising:

(a) a matrix resin component, comprising:

- i. from 10 to about 80 weight percent of an \*\*epoxy\*\* resin component;
- ii. from 10 to about 50 weight percent of a prereact component; and
- iii. from 0.8 to about 1.6 equivalents, based upon the \*\*epoxy\*\* groups in components (a) and (b), of an aromatic diamine \*\*curing\*\* \*\*agent\*\*;

wherein said prereact component (ii) is essentially phenolic hydroxyl-group free wherein the \*\*molecular\*\* \*\*weight\*\* of component (ii) is such that phase separation does not result upon cure of the heat-curable resin system; and wherein. . .

CLAIMS:

CLMS (18)

18. . . . heat curable prepreg comprising:

(a) a matrix resin component, comprising:

- i. from 10 to about 80 weight percent of an \*\*epoxy\*\* resin component;
- ii. from 10 to about 50 weight percent of a prereact component; and
- iii. from 0.8 to about 1.6 equivalents, based upon the \*\*epoxy\*\* groups in components (a) and (ii), of an aromatic diamine \*\*curing\*\* \*\*agent\*\*;

wherein said prereact component (ii) is the essentially phenolic hydroxyl-free reaction product of an \*\*epoxy\*\* resin and a diphenol; wherein the \*\*molecular\*\* \*\*weight\*\* of component (ii) is such that phase separation does not result upon cure of the heat-curable resin system; and wherein. . . .

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(FILE 'USPAT' ENTERED AT 11:32:55 ON 15 JUL 1997)

L1 1 S 5335004/PN  
L2 268 S BISPHENOL AF  
L3 79 S L2 AND EPOXY?  
L4 44 S L3 AND MOLECULAR WEIGHT  
L5 0 S L4 AND (MOLECULAR WEIGHT (2A) EPOXY?)  
L6 13 S L4 AND (MOLECULAR WEIGHT (P) EPOXY?)  
L7 7 S L6 AND CURING AGENT

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US PAT NO: 5,059,512 [IMAGE AVAILABLE]  
DATE FILED: Oct. 10, 1989  
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L28: 5 of 5

US PAT NO: 5,059,512 [IMAGE AVAILABLE]

L28: 5 of 5

**ABSTRACT:**

An . . . . 4; and is n being 1 to 2; and onium salt; and an organic solvent. The composition is used for \*\*cationic\*\* \*\*polymerization\*\* of \*\*cationic\*\* \*\*polymerizable\*\* materials including in the formation of a pattern of a photoresist. Also certain novel epoxy-functionalized organosilicons are provided that are. . . .

**SUMMARY:**

BSUM(3)

The present invention is concerned with ultraviolet sensitive photoinitiator composition. The compositions of the present invention are especially useful for promoting \*\*cationic\*\* \*\*polymerizations\*\*. In particular, the compositions of the present invention find particular applicability in the formation of patterns of photoresists employing imagewise. . . . photospeed. Also the photoinitiator compositions of the present invention are useful for initiating the polymerization of a wide variety of \*\*cationic\*\* \*\*polymerizable\*\* monomers and polymers.

**SUMMARY:**

BSUM(6)

Various compounds have been suggested as photoinitiators for photochemically induced \*\*cationic\*\* \*\*polymerizations\*\* of such materials as epoxy resins, cyclic ethers, cyclic esters, such as cyclic formals and cyclic acetals, polyvinyl acetals, phenoplasts,. . . .

**SUMMARY:**

BSUM(7)

Along these lines, see U.S. Pat. No. 4,161,478 to Crivello, and Watt, et al., "A Novel Photoinitiator of \*\*Cationic\*\* \*\*Polymerization\*\*: Preparation and Characterization of Bis[4-(diphenylsulfonio)phenyl]sulfide-Bis-Hexafluorophosphate", Journal of Polymer Science: Polymer Chemistry Edition, Vol. 22, p. 1789, 1980 John Wiley & . . .

**SUMMARY:**

· BSUM(8)

Certain sulfonium and iodonium salts have been suggested as the initiators for such \*\*cationic\*\* \*\*polymerizations\*\*. Additional discussions concerning these previously suggested sulfonium and iodonium salts can be found, for instance, in Pappas, et al., "Photoinitiation of \*\*Cationic\*\* \*\*Polymerization\*\*. III. Photosensitization of Diphenyliodonium and Triphenylsulfonium Salts", Journal of Polymer Science: Polymer Chemistry Edition, Vol. 22, pp. 77-84, 1984 John Wiley & Sons, Inc.; Crivello, et al., "Photoinitiated \*\*Cationic\*\* \*\*Polymerization\*\* with Triarylsulfonium Salts", Journal of Polymer Science: Polymer Chemistry Edition, Vol. 17, pp. 977-999, 1979 John Wiley & Sons, Inc.; . . . Photoinitiators", Journal of Polymer Science: Polymer Chemistry Edition, Vol. 18, pp. 2677-2695, 1980 John Wiley & Sons, Inc.; and Crivello, "\*\*Cationic\*\* \*\*Polymerization\*\*--Iodonium and Sulfonium Salt Photoinitiators", Advances in Polymer Science, Series #62, pp. 1-48.

SUMMARY:

BSUM(10)

Although various of the prior art onium salts are very efficient photoinitiators for a wide range of \*\*cationic\*\* \*\*polymerizable\*\* materials, such suffer from the deficiency that ultraviolet light absorption in the 300-400 nanometer range is lacking. This range, however, . . .

SUMMARY:

BSUM(14)

In particular, the present invention is concerned with light sensitive photoinitiator compositions that are especially suitable for \*\*cationic\*\* \*\*polymerizations\*\*. The compositions of the present invention contain:

SUMMARY:

BSUM(22)

A) a \*\*cationically\*\* \*\*polymerizable\*\* material;

SUMMARY:

BSUM(23)

B) an onium salt in an amount sufficient to cause polymerization of the \*\*cationically\*\* \*\*polymerizable\*\* material; and

SUMMARY:

BSUM(26)

- 1) a \*\*cationic\*\* \*\*polymerizable\*\* material;

SUMMARY:

BSUM(27)

- 2) an onium salt in an amount sufficient to cause polymerization of the \*\*cationic\*\* \*\*polymerizable\*\* material; and

SUMMARY:

BSUM(30)

The uncured film is imagewise exposed to ultraviolet light in a pattern to thereby cause \*\*cationic\*\* \*\*polymerization\*\* of the film in the exposed pattern. The photoresist is then developed by removing the unexposed portion of the film.

DETDESC:

DETD(29)

In . . . order to facilitate a mixture of the components of the above compositions with a polymerizable composition for use of the \*\*initiator\*\*.

DETDESC:

DETD(32)

The light sensitive compositions of the present invention are useful as photoinitiators for \*\*cationic\*\* \*\*polymerizations\*\* such as polymerizations of epoxy polymers, phenoplast, aminoplast, polyvinylacetals, lactones, cyclic ethers, and cyclic esters such as cyclic acetates and. . . .

DETDESC:

DETD(33)

Typical . . . of epoxy polymers include the epoxidized novolak polymers and the polyepoxides from halo-epoxy alkanes such as epichlorohydrin and a polynuclear \*\*dihydric\*\* \*\*phenol\*\* such as bisphenol A. Mixtures of epoxides can be used when desired.

DETDESC:

DETD(38)

Examples of polynuclear dihydroxy \*\*phenols\*\* are those having the formula: ##STR20## wherein Ar is an aromatic divalent hydrocarbon such as naphthylene and, preferably, phenylene; A. . . can be the same or different are alkyl radicals, preferably having from 1 to 4 carbon atoms, halogen atoms, i.e., \*\*fluorine\*\*, chlorine, bromine, and iodine, or alkoxy radicals, preferably having from 1 to 4 carbon atoms; x and y are integers. . .

DETDESC:

DETD(40)

The . . . from 1 to 3 carbon atoms, and cycloalkylene radicals having up to and including 10 carbon atoms. The most preferred \*\*dihydric\*\* \*\*phenol\*\* is bisphenol A, i.e., 2,2'-bis(p-hydroxyphenyl)propane.

DETDESC:

DETD(44)

In addition, the polyepoxides of halo epoxy alkane of the type discussed above and a polynuclear \*\*dihydric\*\* \*\*phenol\*\* of the type above can be employed. The preferred polyepoxides of this class being the polyepoxides of epichlorohydrin and bisphenol. . .

DETDESC:

DETD(45)

The \*\*initiator\*\* compositions of the present invention are especially suitable in polymerizations of organosilicon resins and most particularly the polysilsesquioxane prepolymers such. . .

DETDESC:

DETD(54)

In \*\*cationic\*\* \*\*polymerizations\*\*, the onium salts are generally employed in amounts of about 0.5 to about 10% by weight and preferably about 4. . .

DETDESC:

• DETD (55)

The \*\*cationic\*\* \*\*polymerizable\*\* compositions can also include conventional additives such as filter, plasticizers, and diluents.

DETDESC:

DETD (58)

The compositions after being applied to the desired substrate are imagewise exposed to ultraviolet light radiation in the near \*\*UV\*\* range of about 300 to about 400 nanometers at dosages of about 20 to about 100 millejoules/cm.<sup>2</sup>. The compositions are. . .

CLAIMS:

CLMS (1)

What is claimed is:

1. An ultraviolet light sensitive photoinitiator composition suitable for \*\*cationic\*\* \*\*polymerization\*\* reactions which comprises:
  - A) at least one anthracene derivative represented by the formula: ##STR34## wherein X is CH.dbd.CH.<sub>2</sub> or --(--CH.<sub>2</sub>). . .

CLAIMS:

CLMS (7)

7. An ultraviolet light sensitive composition comprising:
  - A) a \*\*cationically\*\* \*\*polymerizable\*\* material;
  - B) an onium salt in an amount sufficient to cause polymerization of the \*\*cationically\*\* \*\*polymerizable\*\* material; and
  - C) an anthracene derivative represent by the formula: ##STR38## wherein X is CH.dbd.CH.<sub>2</sub> or --(--CH.<sub>2</sub>. --).sub.n O--(--R) with R. .

CLAIMS:

CLMS (13)

13. The compositions of claim 7 wherein said \*\*cationically\*\* \*\*polymerizable\*\* material is an epoxy polymer.

CLAIMS:

CLMS (14)

14. The compositions of claim 7 wherein said \*\*cationically\*\*  
\*\*polymerizable\*\* material is a silicone polymer.

=>

## SUMMARY:

BSUM(29)

The . . . oxypropylenealkylether groups are readily obtainable by reacting partially fluorinated or perfluorinated aliphatic or aromatic carboxylic acids or isocyanates with polyoxypropylene \*\*glycol\*\* monoalkyl ethers, possess, in comparison with the comb polymers likewise suitable but difficult to prepare and consisting of a polyacrylate. . .

## SUMMARY:

BSUM(42)

The . . . perfluorinated aromatic carboxylic acids or perfluoroalkyl-substituted aromatic carboxylic acids or the corresponding carboxylic acid derivatives, preferably carbonyl chlorides, with polyoxypropylene \*\*glycol\*\* monoalkyl ethers having molecular weights of from 148 to 4134, preferably from 322 to 1524, which in turn are obtained. . . 4 carbon atoms, for example the corresponding methyl, ethyl, isopropyl or 2-hydroxyethyl esters, and are transesterified with the abovementioned polyoxypropylene \*\*glycol\*\* monoalkyl ethers. The addition reaction of the polyoxypropylene \*\*glycol\*\* monoalkyl ethers with partially fluorinated or perfluorinated, aliphatic or aromatic isocyanates proceeds particularly advantageously, so that this process is preferred. . .

## SUMMARY:

BSUM(43)

Components . . . C.<sub>sub.6</sub> F.<sub>sub.13</sub> --CH.<sub>sub.2</sub> --, C.<sub>sub.6</sub> F.<sub>sub.5</sub> -- or CF.<sub>sub.3</sub> --C.<sub>sub.6</sub> H.<sub>sub.4</sub> --, and particularly useful and therefore preferably used polyoxypropylene \*\*glycol\*\* monoalkyl ethers are polyoxypropylene \*\*glycol\*\* monomethyl ethers having a molecular weight of from 380 to 1366.

## SUMMARY:

BSUM(61)

Suitable . . . are preferably used, and in particular adipic acid. Examples of dihydric and polyhydric alcohols, in particular diols, are: ethanediol, diethylene \*\*glycol\*\*, 1,2- and 1,3-propanediol, dipropylene

\*\*glycol\*\*, 1,4-butanediol, 1,5-pantanediol, 1,6-hexanediol, 1,10-decanediol, glycerol and trimethylolpropane. Ethanediol, diethylene \*\*glycol\*\*, 1,4-butanediol, 1,5-pantanediol, 1,6-hexanediol or mixtures of at least two of the stated diols, in particular mixtures of 1,4-butanediol, 1,5-pantanediol and. . .

SUMMARY:

BSUM(65)

However, . . . as sodium methylate, sodium ethylate, potassium ethylate or potassium isopropylate, as catalysts and with the addition of at least one \*\*initiator\*\* molecule which contains from 2 to 8, preferably from 2 to 6, bonded reactive hydrogen atoms, or by \*\*cationic\*\* \*\*polymerization\*\* using Lewis acids, such as antimony pentachloride, boron fluoride etherate, etc., or bleaching earth as catalysts, from one or more. . .

SUMMARY:

BSUM(66)

Examples . . . 1,2-propylene oxide. The alkylene oxides can be used individually, alternately one after the other or as mixtures. Examples of suitable \*\*initiator\*\* molecules are water, organic dicarboxylic acids, such as succinic acid, adipic acid, phthalic acid and terephthalic acid, aliphatic and aromatic,. . .

SUMMARY:

BSUM(67)

Other suitable \*\*initiator\*\* molecules are alkanolamines, dialkanolamines and/or trialkanolamines, such as ethanolamine, diethanolamine, N-methyl- and N-ethylethanolamine, N-methyl- and N-ethyldiethanolamine and triethanolamine, and ammonia. Polyhydric, in particular dihydric and/or trihydric, alcohols, such as ethanediol, 1,2- and 1,3-propanediol, diethylene \*\*glycol\*\*, dipropylene \*\*glycol\*\*, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose, are preferably used.

SUMMARY:

BSUM(71)

Examples of suitable hydroxyl-containing polyacetals are the compounds which can be prepared from glycols, such as diethylene \*\*glycol\*\*,

triethylene \*\*glycol\*\*, 4,4'-dihydroxyethoxydiphenyldimethylmethane or hexanediol, and formaldehyde. Suitable polyacetals can also be prepared by polymerization of cyclic acetals.

SUMMARY:

BSUM(72)

Suitable . . . of the conventional type, which can be prepared, for example, by reacting diols, such as 1,3-propanediol, 1,4-butanediol and/or 1,6-hexanediol, diethylene \*\*glycol\*\*, triethylene \*\*glycol\*\* or tetraethylene \*\*glycol\*\*, with diaryl carbonates, e.g. diphenyl carbonate or phosgene.

SUMMARY:

BSUM(74)

c) . . . 300. For example, aliphatic, cycloaliphatic and/or araliphatic diols of 2 to 14, preferably 4 to 10, carbon atoms, e.g. ethylene \*\*glycol\*\*, 1,3-propanediol, 1,10-decanediol, n-, m- and p-dihydroxycyclohexane, diethylene \*\*glycol\*\*, dipropylene \*\*glycol\*\* and, preferably, 1,4-butanediol, 1,6-hexanediol and bis-(2-hydroxyethyl)-hydroquinone, triols, such as 1,2,4- and 1,3,5-trihydroxycyclohexane, glycerol and trimethylolpropane, and low molecular weight hydroxyl-containing polyalkylene oxides based on ethylene oxide and/or 1,2-propylene oxide, and the abovementioned diols and/or triols are suitable as \*\*initiator\*\* molecules.

DETDESC:

DETD(4)

33.6 parts by weight of polyoxypropylene \*\*glycol\*\* monomethyl ether having an OH number of 144 and prepared by anionic polyaddition of 1,2-propylene oxide with methanol were cooled. . . .

DETDESC:

DETD(6)

After . . . (about 100 mbar). The residue obtained comprised 54.4 parts by weight (93% by weight of theory) of the desired polyoxypropylene \*\*glycol\*\* monomethyl ether perfluorobutyrate in the form of a clear liquid having a \*\*fluorine\*\* content of 22.3% by weight. The theoretical \*\*fluorine\*\* content is 22.4% by weight.

DETDESC:

DETD(8)

The . . . similarly to Example 1, except that the following starting materials and amounts were used: 32.3 parts by weight of polyoxypropylene \*\*glycol\*\* monomethyl ether having a hydroxyl number of 79 and prepared by anionic polyaddition of 1,2-propylene oxide with methanol,

DETDESC:

DETD(11)

44.2 parts by weight (91% of theory) of the desired polyoxypropylene \*\*glycol\*\* monomethyl ether perfluorohexylacetate were obtained in the form of a reddish brown, slightly viscous liquid having a \*\*fluorine\*\* content of 22.2% by weight. The theoretical \*\*fluorine\*\* content is 23.0% by weight.

DETDESC:

DETD(13)

The . . . similarly to Example 1, except that the following starting materials and amounts were used: 47.4 parts by weight of polyoxypropylene \*\*glycol\*\* monomethyl ether having a hydroxyl number of 79 and prepared by anionic polyaddition of 1,2-propylene oxide with methanol,

DETDESC:

DETD(15)

56.5 parts by weight (94% by weight of theory) of the desired polyoxypropylene \*\*glycol\*\* monomethyl ether pentafluorobenzoate were obtained in the form of a reddish brown liquid having a \*\*fluorine\*\* content of 10.1% by weight. The theoretical \*\*fluorine\*\* content is 10.5% by weight.

DETDESC:

DETD(17)

18.7 . . . atmosphere of dry nitrogen at 25.degree. C. in the course of 20 minutes, to parts by weight of a polyoxypropylene \*\*glycol\*\* monomethyl ether having a hydroxyl number of 41 and prepared by anionic polyaddition of 1,2-propylene oxide with methanol.

DETDESC:

DETD(18)

The . . . then heated to 70.degree. C. and the reaction was completed at this temperature by stirring for two hours. The polyoxypropylene \*\*glycol\*\* monomethyl ether N-(3-trifluoromethylphenyl)-carbamate was obtained in the form of a clear, yellowish liquid having a \*\*fluorine\*\* content of 3.6% by weight. The theoretical \*\*fluorine\*\* content is 3.64% by weight.

DETDESC:

DETD(21)

A . . . a polyoxypropylenepolyol having a hydroxyl number of 400 and prepared by anionic polyaddition of 1,2-propylene oxide with sucrose as the \*\*initiator\*\* molecule, 40 parts by weight of perfluorohexane and 0.5 part by weight of a polyoxypropylene \*\*glycol\*\* monomethyl ether perfluorobutyrate, prepared similarly to Example 1 from a polyoxypropylene \*\*glycol\*\* monomethyl ether having a hydroxyl number of 79 and perfluorobutyryl chloride, was mixed thoroughly with a high speed stirrer (2000. . . .

DETDESC:

DETD(27)

When the procedure described in Example 5 was followed but 0.5 part by weight of polyoxypropylene \*\*glycol\*\* monomethyl ether pentafluorobenzoate, prepared as described in Example 3, was used instead of the polyoxypropylene \*\*glycol\*\* monomethyl ether perfluorobutyrate, a stable emulsion which contained no free perfluorohexane and showed no signs of separation after a storage. . . .

DETDESC:

DETD(29)

A . . . a polyoxypropylenepolyol having a hydroxyl number of 400 and prepared by anionic polyaddition of 1,2-propylene oxide with sucrose as the \*\*initiator\*\* molecule, 40 parts by weight of perfluorohexane, 1.0 part by weight of a hydrophilic polysiloxane having polyether side chains (Tegostab.RTM. B8406 from Goldschmidt AG, Essen) and 0.5 part by weight of polyoxypropylene \*\*glycol\*\* monomethyl ether pentafluorobenzoate prepared as described in Example 3 was mixed thoroughly at 23.degree. C. with a high speed stirrer. . . .

DETDESC:

DETD(32)

A . . . . a polyoxypropylenepolyol having a hydroxyl number of 400 and prepared by anionic polymerization of 1,2-propylene oxide with sucrose as the \*\*initiator\*\* molecule, 40 parts by weight of perfluorohexane and 1.0 part by weight of a hydrophilic polysiloxane having polyether side chains. . .

DETDESC:

DETD(37)

The . . . . a polyoxypropylenepolyol having a hydroxyl number of 400 and prepared by anionic polyaddition of 1,2-propylene oxide with sucrose as the \*\*initiator\*\* molecule, 1.6 parts by weight of water and 2.1 parts by weight of N,N-dimethylcyclohexylamine and 2.0 parts by weight of. .

DETDESC:

DETD(43)

. . . .  
fine-celled

- 10 Carboxylic ester prepared similarly to Example 1 from  
1.64 Very fine-celled  
perfluorobutyryl chloride and a polyoxypropylene \*\*glycol\*\*  
monomethyl ether having a hydroxyl number of 79
- 11 Carboxylic ester prepared similarly to Example 2 from  
0.26 Excellent by  
perfluorohexylacetyl chloride and a polyoxypropylene  
fine-celled  
\*\*glycol\*\* monomethyl ether having a hydroxyl number of  
144
- 12 Carboxylic ester according to Example 2  
0.26 Very fine-celled. . .
- 13 Carboxylic ester prepared similarly to Example 2 from  
0.26 Very fine-celled  
perfluorohexylacetyl chloride and a polyoxypropylene  
\*\*glycol\*\* monomethyl ether having a hydroxyl number of 41
- 14 Carboxylic ester according to Example 3  
0.26 Very fine-celled
15. . . Carbamic ester prepared similarly to Example 4 from  
0.26 Very fine-celled  
3-trifluoromethylphenyl isocyanate and a polyoxy-  
propylene \*\*glycol\*\* monomethyl ether having a hydroxyl

number of 144

16 Carbamic ester prepared similarly to Example 4 from  
0.55 Very fine-celled  
3-trifluoromethylphenyl isocyanate and a polyoxy-  
propylene \*\*glycol\*\* monomethyl ether having a hydroxyl  
number of 79

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-  
DETDESC:

DETD(45)

20 . . . a polyoxypropylenepolyol having a hydroxyl number of 400 and prepared by anionic polyaddition of 1,2-propylene oxide with sucrose as the \*\*initiator\*\* molecule, 1.6 parts by weight of water, 2.1 parts by weight of N,N-dimethylcyclohexylamine and 2.0 parts by weight of a. . .

DETDESC:

DETD(56)

21 . . . of 58.4 parts by weight of a polyoxypropylenepolyol having a hydroxyl number of 490 and prepared using sorbitol as the \*\*initiator\*\* molecule, 8.0 parts by weight of glycerol, 11.1 parts by weight of dipropylene \*\*glycol\*\*, 1.9 parts by weight of diethanolamine, 14.0 parts by weight of .beta.-trichloroethyl phosphate, 1.6 parts by weight of N,N-dimethylcyclohexylamine, 3.2. . . a polysiloxane having polyether side chain (Tegostab.RTM. B 8406 from Goldschmidt AG, Essen) and 1.8 parts by weight of polyoxypropylene \*\*glycol\*\* monomethyl ether perfluorobutyrate, prepared as described in Example 1. The stable emulsion was then mixed thoroughly at 23.degree. C. with. . .

DETDESC:

DETD(59)

2 . . . in a pressure-tight vessel, in a mixture which consisted of 70.4 parts by weight of a polyoxypropylene (80) polyoxyethylene (20) \*\*glycol\*\* having a hydroxyl number of 30 and prepared using 1,3-propanediol as the \*\*initiator\*\*, 17.5 parts by weight of a polyoxypropylene (80) polyoxyethylene (20) polyol having a hydroxyl number of 35 and prepared using glycerol as the \*\*initiator\*\*, 9.2 parts by weight of 1,4-butanediol, 0.1 part by weight of a polysiloxane having polyether side chains (DC 193 from. . . strength solution of triethylenediamine in 1,4-butanediol, 0.02 part by weight of dibutyltin dilaurate and 1.0 part by weight of polyoxypropylene \*\*glycol\*\*

monomethyl ether perfluorohexylacetate, prepared as described in Example 2. The resulting emulsion was then mixed thoroughly at 23.degree. C. with. . . a urethane-containing polyisocyanate having an NCO content of 23% by weight and prepared by reacting diphenylmethane 4,4'-diisocyanate with a polyoxypropylene \*\*glycol\*\* having a molecular weight of 400 and the reaction mixture was introduced into an open mold and allowed to expand. . .

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US PAT NO: 4,929,667 [IMAGE AVAILABLE]

L36: 3 of 3

ABSTRACT:

A urethane prepolymer composition is provided comprising (a) a terminal isocyanate group-containing urethane prepolymer derived from a polytetramethylene \*\*glycol\*\* having a specific molecular weight of 700 to 1500 and an aliphatic and/or alicyclic diisocyanate and (b) a terminal isocyanate group-containing urethane prepolymer derived from a polycaprolactone \*\*diol\*\* and/or polyol having a specific molecular weight of 500 to 1500 and an aliphatic and/or alicyclic diisocyanate, the weight ratio of (a) to (b) being in the range of 80/20 to 20/80. This composition has excellent compatibility with a \*\*diol\*\* compound and/or a polyol compound, and can be formulated together with the \*\*diol\*\* compound and/or the polyol compound into a polyurethane coating composition system which forms a coating film having not only excellent.

SUMMARY:

BSUM(3)

The . . . a urethane prepolymer composition which comprises in specific weight proportions a terminal isocyanate group-containing urethane prepolymer derived from a polytetramethylene \*\*glycol\*\* having a specific molecular weight and a terminal isocyanate group-containing urethane prepolymer derived from a terminal hydroxyl group-containing polycaprolactone having. . . .

SUMMARY:

BSUM(7)

In Japanese Patent Application Laid-Open Specification No. 58-32662, it was proposed to add a polycaprolactone \*\*diol\*\* or polyol as an additive to the so-called two-pack polyurethane coating composition system which is suited for use in coating. . . . used for coating a resin product, such as a polyurethane bumper. In this coating composition system, in addition to the \*\*diol\*\* or polyol to be used as a main component (such as an acrylic polyol and a polyester \*\*diol\*\* or polyol) and the so-called \*\*curing\*\* \*\*agent\*\* (such as an isocyanurate trimer of 1,6-hexamethylene diisocyanate, a biuret adduct of 1,6-hexamethylene diisocyanate, and an isocyanurate trimer of isophorone diisocyanate), a polycaprolactone \*\*diol\*\* or polyol is employed as an additive. Since the additive also has a hydroxyl group, it is necessary to adjust the ratio

of the main component \*\*diol\*\* or polyol to the \*\*curing\*\* \*\*agent\*\* in accordance with the amount of the additive so as to maintain the NCO/OH ratio at an appropriate value. This is not facile and is likely to cause the NCO/OH ratio to be inappropriate. In addition, the polycaprolactone \*\*diol\*\* or polyol is effective for improving the elastic properties at low temperatures of the coating derived from the composition, only when the \*\*diol\*\* or polyol is added in a large amount. However, the addition of the polycaprolactone \*\*diol\*\* or polyol in a large amount is likely to cause the coating derived from the composition to have poor weathering.

SUMMARY:

BSUM(8)

In . . . Japanese Patent Application Publication Specification No. 62-53525, it is described that a linear polyurethane elastomer produced by reacting a copolymer \*\*diol\*\* or polyol derived from a polytetramethylene \*\*glycol\*\* and a caprolactone with a diisocyanate has excellent hydrolysis resistance and low-temperature physical properties. However, this linear polyurethane elastomer cannot. . .

SUMMARY:

BSUM(9)

Japanese Patent Application Laid-Open Specification No. 61-12753 discloses a urethane prepolymer obtained by reacting a polycaprolactone \*\*diol\*\* or polyol having a specific number average molecular weight with an aliphatic or alicyclic diisocyanate. The specification also discloses that. . .

SUMMARY:

BSUM(10)

Japanese Patent Application Laid-Open Specification No. 54-60395 discloses a urethane prepolymer produced by reacting a polytetramethylene \*\*glycol\*\* with a diisocyanate at an NCO/OH equivalent ratio of 2. However, this prepolymer disadvantageously has high viscosity so that the processing thereof is difficult. In addition, the prepolymer has poor compatibility with a \*\*diol\*\* or polyol.

SUMMARY:

BSUM(13)

The . . . As a result, the present inventors have unexpectedly found that a mixture of a urethane prepolymer derived from a polytetramethylene \*\*glycol\*\* having a specific molecular weight and a urethane prepolymer derived from a polycaprolactone \*\*diol\*\* or polyol having a specific molecular weight in specific weight proportions has good compatibility with a \*\*diol\*\* or polyol, and can be formulated together with the \*\*diol\*\* or polyol into an advantageous polyurethane coating composition system capable of forming a coating film which is excellent not only. . .

DETDESC:

DETD (3)

(a) a terminal isocyanate group-containing urethane prepolymer obtained by reacting a polytetramethylene \*\*glycol\*\* having a number average molecular weight of from 700 to 1500 with at least one diisocyanate selected from the group. . . an alicyclic diisocyanate at an equivalent ratio of the isocyanate groups of said diisocyanate to the hydroxyl groups of said \*\*glycol\*\* of at least 5/1, and

DETDESC:

DETD (4)

(b) . . . one polycaprolactone having at least two terminal hydroxyl groups, the polycaprolactone being selected from the group consisting of a polycaprolactone \*\*diol\*\* and a polycaprolactone polyol each having a number average molecular weight of from 500 to 1500, with at least one. . .

DETDESC:

DETD (9)

(a) a terminal isocyanate group-containing urethane prepolymer obtained by reacting a polytetramethylene \*\*glycol\*\* having a number average molecular weight of from 700 to 1500 with at least one diisocyanate selected from the group. . . an alicyclic diisocyanate at an equivalent ratio of the isocyanate groups of said diisocyanate to the hydroxyl groups of said \*\*glycol\*\* of at least 5/1, and

DETDESC:

DETD (10)

(b) . . . one polycaprolactone having at least two terminal hydroxyl groups, the polycaprolactone being selected from the group consisting of a polycaprolactone \*\*diol\*\* and a polycaprolactone polyol each

having a number average molecular weight of from 500 to 1500 with at least one. . .

DETDESC:

DETD(12)

(B) at least one compound having at least two hydroxyl groups, the compound being selected from the group consisting of a \*\*diol\*\* compound and a polyol compound,

DETDESC:

DETD(14)

In . . . consisting of an aliphatic diisocyanate and an alicyclic diisocyanate is used as the material to be reacted with a polymethylene \*\*glycol\*\* and with at least one polycaprolactone having at least two terminal hydroxyl groups for preparing prepolymers (a) and (b), respectively. . . .

DETDESC:

DETD(16)

Various . . . urethane prepolymer of polyether type. For example, a homopolymer or copolymer of ethylene oxide or propylene oxide and a polytetramethylene \*\*glycol\*\* obtained by polymerization of tetrahydrofuran have been employed. However, in the present invention, it is essential to employ polytetramethylene \*\*glycol\*\* having a number average molecular weight of 700 to 1500 as a material for preparing prepolymer (a). The use of such a specific polytetramethylene \*\*glycol\*\* is advantageous for obtaining an ultimate coating film which is not only excellent in water resistance and elastic recovery but. . . . that it has excellent low-temperature physical properties, such as excellent elongation, impact strength and flexibility at low temperatures. The polytetramethylene \*\*glycol\*\* to be used in the present invention must have a number average molecular weight of from 700 to 1500, as mentioned above. The determination method of the number average molecular weight of the polytetramethylene \*\*glycol\*\* is described later. When a polytetramethylene \*\*glycol\*\* having a number average molecular weight of less than 700 is used, the ultimate coating film is poor in elongation at low temperatures. On the other hand, when a polytetramethylene \*\*glycol\*\* having a number average molecular weight of greater than 1500 is used, the resulting urethane prepolymer composition has low NCO. . . .

DETDESC:

DETD(17)

The polytetramethylene \*\*glycol\*\* to be used in the present invention may preferably be produced by \*\*cationic\*\* \*\*polymerization\*\* of tetrahydrofuran in the presence of a catalyst. As the catalyst, there may be used acetic anhydride-perchloric acid, fluorosulfonic acid, fuming sulfuric acid and the like. In particular, the polytetramethylene \*\*glycol\*\* may be produced as follows. Fluorosulfonic acid is added to tetrahydrofuran in an amount of about 1 to 30% by. . . minutes to several tens of hours so that the reaction is allowed to proceed. The molecular weight of the polytetramethylene \*\*glycol\*\* can be regulated by controlling the reaction conditions, such as reaction temperature, reaction period and the amount of catalyst. Commercially. . .

DETDESC:

DETD(18)

On . . . production of a urethane prepolymer of polyester type. For example, polyester diols or polyols, such as those produced from a \*\*glycol\*\* (e.g., ethylene \*\*glycol\*\*, 1,4-butylene \*\*glycol\*\* and 1,6-hexylene \*\*glycol\*\*) and an acid (e.g., adipic acid and isophthalic acid) have been employed. However, in the present invention, it is essential. . . employ at least one polycaprolactone having at least two terminal hydroxyl groups selected from the group consisting of a polycaprolactone \*\*diol\*\* and a polycaprolactone polyol each having a number average molecular weight of from 500 to 1500 as a material for. . . in water resistance and weathering resistance. In the present invention, the number average molecular weight of each of the polycaprolactone \*\*diol\*\* and polyol is in the range of from 500 to 1500, as mentioned above. The determination method of the number average molecular weight of the polycaprolactone \*\*diol\*\* and polyol is described later. When a polycaprolactone \*\*diol\*\* or a polycaprolactone polyol each having a number average molecular weight of less than 500 is used, the ultimate coating film is poor in elongation at low temperatures. On the other hand, when a polycaprolactone \*\*diol\*\* or a polycaprolactone polyol each having a number average molecular weight of more than 1500 is used, the resulting urethane. . .

DETDESC:

DETD(19)

The polycaprolactone to be used in the present invention is a \*\*diol\*\* having two functional hydroxyl groups or a polyol having at least three functional hydroxyl groups or a mixture thereof. Generally, . . .

DETDESC:

DETD(20)

The polycaprolactone \*\*diol\*\* and polycaprolactone polyol to be used in the present invention may be prepared by subjecting .epsilon.-caprolactone to a ring-opening polymerization in the presence of a catalyst and using, as an \*\*initiator\*\*, a dihydric or polyhydric alcohol. Examples of catalysts include organic titanium compounds, such as tetrabutyltitanate, tetrapropyltitanate and tetraethyltitanate; tin compounds, . . . oxide, dibutyltin dilaurate, tin chloride and tin bromide; and the like. Examples of initiators include dihydric alcohols, such as ethylene \*\*glycol\*\*, propylene \*\*glycol\*\*, 1,3-butylene \*\*glycol\*\* and neopentyl \*\*glycol\*\*; trihydric alcohols, such as trimethylolpropane and glycerin; and other polyhydric alcohols such as pentaerythritol. From the viewpoint of obtaining prepolymer. . . . ring-opening polymerization of .epsilon.-caprolactone is preferably conducted in an atmosphere of nitrogen gas. The molar ratio of .epsilon.-caprolactone to an \*\*initiator\*\* is adjusted so as to obtain a polycaprolactone \*\*diol\*\* or polyol having a predetermined number average molecular weight. The catalyst is added in an amount of 0.1 to 100. . . .

DETDESC:

DETD(21)

In the present invention, the number average molecular weight of each of the polytetramethylene \*\*glycol\*\* and the terminal hydroxyl group-containing polycaprolactone is determined by measuring the hydroxyl value of each of the \*\*glycol\*\* and the polycaprolactone in accordance with the method of Japanese Industrial Standards (JIS) K 1577, section 6.4 and calculating from. . . . is the hydroxyl value and N is the number of hydroxyl groups present in one molecule of each of the \*\*glycol\*\* and the polycaprolactone.

DETDESC:

DETD(22)

In . . . preparing prepolymers (a) and (b), the equivalent ratio of NCO groups of the diisocyanate to OH groups of the polytetramethylene \*\*glycol\*\*, and the equivalent ratio of NCO groups of the diisocyanate to OH groups of the terminal hydroxyl group-containing polycaprolactone, are. . . . ratios do not exceed 40/1. When NCO/OH is less than 5/1, consecutive addition reaction between the diisocyanate and the polytetramethylene \*\*glycol\*\* or the terminal hydroxyl group-containing

polycaprolactone is likely to occur so that a prepolymer having an unfavorably high molecular weight. . . .

DETDESC:

DETD (23)

The reaction of each of the polytetramethylene \*\*glycol\*\* and the polycaprolactone having at least two terminal hydroxyl groups with at least one diisocyanate selected from the group consisting. . . .

DETDESC:

DETD (25)

The terminal isocyanate group-containing prepolymer (a) above obtained by reacting a polytetramethylene \*\*glycol\*\* of specific molecular weight with at least one diisocyanate, is mixed with the terminal isocyanate group-containing prepolymer (b) above obtained. . . .

DETDESC:

DETD (26)

The . . . above. Alternatively, prepolymers (a) and (b) may be prepared simultaneously to obtain an urethane prepolymer composition. That is, the polytetramethylene \*\*glycol\*\* and the terminal hydroxyl group-containing polycaprolactone are mixed in proportions such that the resultant prepolymer composition has a weight ratio. . . . and (b). The equivalent ratio of NCO groups of the diisocyanate to the total of OH groups of the polytetramethylene \*\*glycol\*\* and the terminal hydroxyl group-containing polycaprolactone is at least 5/1, preferably at least 8/1. The upper limit of the equivalent. . . .

DETDESC:

DETD (27)

The . . . composition and (B) at least one compound having at least two hydroxyl groups selected from the group consisting of a \*\*diol\*\* compound and a polyol compound, wherein the equivalent ratio of the total number of the terminal isocyanate groups of (a). . . .

DETDESC:

DETD (28)

Representative examples of hydroxyl groupcontaining compounds include an acrylic polyol, a polyester \*\*diol\*\* or polyol, a polycarbonate \*\*diol\*\* or polyol and a \*\*fluorine\*\*-containing polyol. Of these hydroxyl group-containing compounds, an acrylic polyol is preferred from the viewpoints of compatibility with the present prepolymer. . .

DETDESC:

DETD (37)

As a polymerization catalyst, there may be employed a customary radical polymerization \*\*initiator\*\*, for example, an azo compound, a peroxide, a diazo compound, a redox catalyst or the like.

DETDESC:

DETD (39)

Examples . . . isophthalic acid and terephthalic acid, with at least one dihydric or polyhydric alcohol selected from the group consisting of ethylene \*\*glycol\*\*, propylene \*\*glycol\*\*, diethylene \*\*glycol\*\*, butylene \*\*glycol\*\*, neopentyl \*\*glycol\*\* trimethylolpropane and glycerin; and polycaprolactone diols or polyols obtained by a ring opening polymerization of .epsilon.-caprolactone using a dihydric or. .

DETDESC:

DETD (49)

The . . . (b) with (B) at least one compound having at least two hydroxyl groups selected from the group consisting of a \*\*diol\*\* compound and a polyol compound.

DETDESC:

DETD (50)

As mentioned hereinbefore, it was proposed to add a polycaprolactone \*\*diol\*\* or polyol as an additive to the so-called two-pack polyurethane coating composition system which is suited for use in coating. . . and weathering resistance. By contrast, in the present invention, a urethane prepolymer composition comprising a prepolymer derived from a polytetramethylene \*\*glycol\*\* having a specific molecular weight and a prepolymer derived from a terminal hydroxyl group-containing polycaprolactone is used and any additional \*\*diol\*\* or polyol as employed in the prior art is not used. By the use of such a specific

prepolymer composition. . .

DETDESC:

DETD(51)

With . . . the coating film is subjected to acid decomposition or alkali decomposition and the resultant decomposition products, such as diamine, 1,4-butylene \*\*glycol\*\* and OH(CH<sub>2</sub>).sub.5 COOH, are identified by functional group analysis; or a method in which the coating film is subjected to. . .

DETDESC:

DETD(60)

Reference Example 1 (synthesis of a urethane prepolymer from a polytetramethylene \*\*glycol\*\*)

DETDESC:

DETD(61)

Charged . . . thermometer, a cooling apparatus and an agitator are 1,008 g of 1,6-hexamethylene diisocyanate (HMDI) and 400 g of a polytetramethylene \*\*glycol\*\* having a number average molecular weight of 1,000 (PTG 1000: tradename of a product produced and sold by Hodogaya Chemical. . .

DETDESC:

DETD(64)

Reference Example 11 (synthesis of a urethane prepolymer from a polytetramethylene \*\*glycol\*\* and a polycaprolactone polyol)

DETDESC:

DETD(70)

Reference Example 14 (synthesis of a urethane prepolymer from a polytetramethylene \*\*glycol\*\* and a polycaprolactone polyol)

DETDESC:

DETD(72)

Reference Example 15 (synthesis of a urethane prepolymer from a polytetramethylene \*\*glycol\*\* and a polycaprolactone polyol)

DETDESC:

DETD (74)

Reference Example 16 (synthesis of a urethane prepolymer from a polytetramethylene \*\*glycol\*\* and a polycaprolactone polyol)

CLAIMS:

CLMS (1)

What . . . claimed is:

1. A urethane prepolymer composition comprising:

- (a) a terminal isocyanate group-containing urethane prepolymer obtained by reacting a polytetramethylene \*\*glycol\*\* having a number average molecular weight of from 700 to 1500 with at least one diisocyanate selected from the group . . . an alicyclic diisocyanate at an equivalent ratio of the isocyanate groups of said diisocyanate to the hydroxyl groups of said \*\*glycol\*\* of at least 5/1, and
- (b) a terminal isocyanate group-containing urethane prepolymer obtained by reacting at least one polycaprolactone having at least two terminal hydroxyl groups, said polycaprolactone being selected from the group consisting of a polycaprolactone \*\*diol\*\* and a polycaprolactone polyol each having a number average molecular weight of from 500 to 1500, with at least one. . . .

CLAIMS:

CLMS (6)

6. . . . to claim 1, wherein the equivalent ratio of the isocyanate groups of said diisocyanate to the hydroxyl groups of said \*\*glycol\*\* of (a) and the equivalent ratio of the isocyanate groups of said diisocyanate to the hydroxyl groups of said polycaprolactone. . . .

CLAIMS:

CLMS (7)

7. . . . as follows:

(A) a urethane prepolymer composition comprising:

- (a) a terminal isocyanate group-containing urethane prepolymer obtained by reacting a polytetramethylene \*\*glycol\*\* having a number average

molecular weight of from 700 to 1500 with at least one diisocyanate selected from the group. . . an alicyclic diisocyanate at an equivalent ratio of the isocyanate groups of said diisocyanate to the hydroxyl groups of said \*\*glycol\*\* of at least 5/1, and  
(b) a terminal isocyanate group-containing urethane prepolymer obtained by reacting at least one polycaprolactone having at least two terminal hydroxyl groups, said polycaprolactone being selected from the group consisting of a polycaprolactone \*\*diol\*\* and a polycaprolactone polyol each having a number average molecular weight of from 500 to 1500, with at least one. . .

at least one compound having at least two hydroxyl groups, said compound being selected from the group consisting of a \*\*diol\*\* compound and a polyol compound,  
wherein the equivalent ratio of the total number of the terminal isocyanate groups of (a). . .

=>

=> d l19 1- cit fd

1. 5,597,388, Jan. 28, 1997, Process for fixation of dyes containing at least one polymerizable double bond by means of UV light; Katharina Fritzsche, 8/444, 115.53, 532, 543, 549, 555, 576, 582, 586 [IMAGE AVAILABLE]

US PAT NO: 5,597,388 [IMAGE AVAILABLE] L19: 1 of 20  
DATE FILED: Dec. 2, 1994

2. 5,518,585, May 21, 1996, Neutral sizing agent for base paper stuff with the use of cationic plastics dispersions; Hans U. Huth, et al., 162/168.2, 168.1, 168.3 [IMAGE AVAILABLE]

US PAT NO: 5,518,585 [IMAGE AVAILABLE] L19: 2 of 20  
DATE FILED: Feb. 23, 1995

3. 5,494,777, Feb. 27, 1996, Radiation sensitive resin composition; Shinji Shiraki, et al., 430/270.1, 281.1 [IMAGE AVAILABLE]

US PAT NO: 5,494,777 [IMAGE AVAILABLE] L19: 3 of 20  
DATE FILED: Apr. 19, 1994

4. 5,346,805, Sep. 13, 1994, Photopolymerizable composition; Syunichi Kondo, et al., 430/281.1, 288.1, 914, 917, 920, 921, 926; 522/25, 31 [IMAGE AVAILABLE]

US PAT NO: 5,346,805 [IMAGE AVAILABLE] L19: 4 of 20  
DATE FILED: Sep. 17, 1993

5. 5,320,769, Jun. 14, 1994, Magnetic paint and magnetic recording medium; Hiroshi Kinoshita, et al., 252/62.54; 427/128; 428/409, 425.9, 694BU, 695 [IMAGE AVAILABLE]

US PAT NO: 5,320,769 [IMAGE AVAILABLE] L19: 5 of 20  
DATE FILED: Apr. 3, 1992

6. 5,250,385, Oct. 5, 1993, Photopolymerizable composition; Syunichi Kondo, et al., 430/192, 281.1, 284.1, 285.1, 287.1; 522/31, 32 [IMAGE AVAILABLE]

US PAT NO: 5,250,385 [IMAGE AVAILABLE] L19: 6 of 20  
DATE FILED: Aug. 30, 1991

7. 5,126,387, Jun. 30, 1992, Flame retardant compositions and method of use; Geoffrey Hand, 524/118; 252/400.2, 400.22, 609; 524/117, 119, 131

[IMAGE AVAILABLE]

US PAT NO: 5,126,387 [IMAGE AVAILABLE] L19: 7 of 20  
DATE FILED: Mar. 1, 1991

8. 5,126,379, Jun. 30, 1992, Esters containing bonded fluorocarbon and oxypropylenealkylether groups, emulsions containing these esters and their use for the preparation of cellular plastics by polyisocyanate polyaddition; Otto Volkert, et al., 521/110; 252/182.22, 182.27; 521/112, 114, 115 [IMAGE AVAILABLE]

US PAT NO: 5,126,379 [IMAGE AVAILABLE] L19: 8 of 20  
DATE FILED: Dec. 18, 1990

9. 5,104,778, Apr. 14, 1992, Silver halide photosensitive material; Junichi Yamanouchi, et al., 430/518, 559, 627, 637, 941 [IMAGE AVAILABLE]

US PAT NO: 5,104,778 [IMAGE AVAILABLE] L19: 9 of 20  
DATE FILED: May 25, 1990

10. 5,032,236, Jul. 16, 1991, Process for producing a surface-blackened steel sheet; Katsushi Saitou, et al., 205/138, 176, 178, 196 [IMAGE AVAILABLE]

US PAT NO: 5,032,236 [IMAGE AVAILABLE] L19: 10 of 20  
DATE FILED: Jun. 21, 1990

11. 4,929,667, May 29, 1990, Urethane prepolymer composition and a polyurethane coating composition system; Kazuki Ban, et al., 524/718; 252/182.22; 524/720, 738, 739; 525/458 [IMAGE AVAILABLE]

US PAT NO: 4,929,667 [IMAGE AVAILABLE] L19: 11 of 20  
DATE FILED: Feb. 1, 1989

12. 4,891,306, Jan. 2, 1990, Photographic light-sensitive silver halide material containing an antistatic block copolymer; Shigeki Yokoyama, et al., 430/527, 528, 529, 631, 634 [IMAGE AVAILABLE]

US PAT NO: 4,891,306 [IMAGE AVAILABLE] L19: 12 of 20  
DATE FILED: Nov. 14, 1988

13. 4,508,916, Apr. 2, 1985, Curable substituted urethane acrylates; Richard G. Newell, et al., 556/420; 522/96, 97; 526/240, 247; 560/26, 115, 158 [IMAGE AVAILABLE]

US PAT NO: 4,508,916 [IMAGE AVAILABLE] L19: 13 of 20  
DATE FILED: May 20, 1983

• 14. 4,464,463, Aug. 7, 1984, Silver halide color photographic light-sensitive material; Tetsuro Kojima, et al., 430/512, 504, 505, 523, 536, 537, 543, 544, 548, 551, 554, 627, 957, 961 [IMAGE AVAILABLE]

US PAT NO: 4,464,463 [IMAGE AVAILABLE] L19: 14 of 20  
DATE FILED: Jul. 26, 1983

15. 4,393,199, Jul. 12, 1983, \*\*Cationic\*\* \*\*polymerization\*\*; Gerald E. Manser, 528/408; 149/19.6; 526/348.7; 528/409, 417, 421 [IMAGE AVAILABLE]

US PAT NO: 4,393,199 [IMAGE AVAILABLE] L19: 15 of 20  
DATE FILED: May 12, 1981

16. 4,366,238, Dec. 28, 1982, Silver halide photographic materials; Shigeki Yokoyama, et al., 430/529, 527, 536, 537, 627, 631, 961 [IMAGE AVAILABLE]

US PAT NO: 4,366,238 [IMAGE AVAILABLE] L19: 16 of 20  
DATE FILED: Jun. 25, 1981

17. 4,123,275, Oct. 31, 1978, Color diffusion transfer photographic materials with vinyl copolymer neutralization rate controlling layer; Yukio Karino, et al., 430/216, 215, 224 [IMAGE AVAILABLE]

US PAT NO: 4,123,275 [IMAGE AVAILABLE] L19: 17 of 20  
DATE FILED: Jul. 26, 1976

18. 4,054,722, Oct. 18, 1977, Acyloxy substituted acrylate timing layers for color diffusion transfer; Takashi Yoshida, et al., 430/454, 215, 216, 449, 463 [IMAGE AVAILABLE]

US PAT NO: 4,054,722 [IMAGE AVAILABLE] L19: 18 of 20  
DATE FILED: Jun. 23, 1976

19. 4,009,129, Feb. 22, 1977, Copolymers of cyclic vinyl ethers and cyclic acetals; Anthony Joseph Papa, et al., 521/103, 172 [IMAGE AVAILABLE]

US PAT NO: 4,009,129 [IMAGE AVAILABLE] L19: 19 of 20  
DATE FILED: May 5, 1975

20. 3,893,985, Jul. 8, 1975, Copolymers of cyclic vinyl ethers and cyclic acetals; Anthony Joseph Papa, et al., 526/266; 549/335, 346, 370, 414, 448 [IMAGE AVAILABLE]

US PAT NO: 3,893,985 [IMAGE AVAILAB

=> d his

(FILE 'USPAT' ENTERED AT 14:36:39 ON 15 JUL 1997)

L1 666 S 4,4-DIAMINODIPHENYLSULFONE  
L2 0 S L1 AND (CATION? (P) 4,4-DIAMINODIPHENYLSULFONE)  
L3 4 S PHENYLPHOSPHONIUM IODIDE  
L4 3 S L3 AND CATION?  
L5 0 S L4 AND (CURE OR CURING OR CURED)  
L6 0 S AROMATIC SUFONIUM SALT?  
L7 9 S SUFONIUM SALT?  
L8 0 S L7 AND L1  
L9 742 S IODONIUM SALT#  
L10 0 S L9 AND L3  
L11 6216 S CATION? POLYMER?  
L12 2085 S L11 AND (INITIATOR OR CURING AGENT)  
L13 109 S CATIONIC POLYMERIZATION INITIATOR  
L14 0 S L13 AND BISPHENOL AF  
L15 2 S L13 AND 347/CLAS  
L16 0 S L15 AND ((FLORINATED) (W) (DIOL OR GLYCOL))  
L17 0 S L12 AND ((FLORINATED) (W) (DIOL OR GLYCOL))  
L18 1224 S L12 AND (DIOL OR GLYCOL)  
L19 20 S L18 AND ((FLUORINE OR FLUORO) (P) (DIOL OR GLYCOL))  
L20 0 S L19 AND (DIPHENOL## OR POLYPHENOL##)  
L21 0 S L19 AND ((POLYHYDRIC## OR DIHYDRIC##) (W) (PHENOL##))  
L22 0 S L19 AND DIHYDROXYBENZENE  
L23 0 S L19 AND (DIPHENOL# OR POLYPHENOL#)  
L24 156 S L12 AND (DIPHENOL## OR POLYPHENOL##)  
L25 2 S L24 AND ((FLUORINE OR FLUORINATED OR FLUORO) (P) (DIPHENOL#))  
OL#  
L26 133 S L12 AND ((POLYHYDRIC OR DIHYDRIC) (W) (PHENOL##))  
L27 10 S L26 AND ((FLUORINE OR FLUORINATE? OR FLUORO) (P) (PHENOL##))  
L28 5 S L27 AND UV  
L29 0 S L28 AND ((DIOL OR GLYCOL) (P) (FLUORINE OR FLUORINATE? OR FLUORO))  
R F  
L30 5 S L28 AND (DIOL# OR GLYCOL#)  
L31 0 S L30 AND ((DIOL# OR GLYCOL#) (P) (FLUORIN? OR FLUORO))  
E CANON KABUSHIKI KAISHA/AS  
L32 15032 S E3  
L33 0 S L32 AND L19  
L34 0 S L19 AND PHOTOLITHOGRAPHY  
L35 0 S L19 AND PLASMA ETCH?  
L36 3 S L19 AND CURING AGENT

=>

## L15 2 L7 AND DIOL?

=> d 115 1-

1. 4,891,417, Jan. 2, 1990, \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers; Alberto Re, et al., 528/112, 402 [IMAGE AVAILABLE]

2. 4,833,227, May 23, 1989, \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers; Alberto Re, et al., 528/73, 103, 104, 108, 110, 401, 402 [IMAGE AVAILABLE]

=> d 2 kwic

US PAT NO: 4,833,227 [IMAGE AVAILABLE] L15: 2 of 2  
TITLE: \*\*Epoxy\*\* resins prepared from perfluoroalkylene telomers

## **ABSTRACT:**

Fluorinated polymers having \*\*epoxy\*\* resin structure, containing at least 10% by weight, preferably 20% by weight, of fluorine, prepared starting from epichlorohydrin and from one or more \*\*diols\*\*, at least one of which is a perfluoroalkylene \*\*diol\*\*, and by using conventional cross-linking agents for \*\*epoxy\*\* resins, such as anhydrides of dicarboxylic acids, di- or tri-isocyanates, polyfunctional amines.

## SUMMARY:

BSUM(2)

The invention relates to fluorinated polymers having \*\*epoxy\*\* resin structure, prepared starting from epichlorohydrin and from one or more \*\*diols\*\*, at least one of which is a perfluoroalkylene \*\*diol\*\*.

## SUMMARY:

BSUM (9)

A is a radical of a fluorinated or non-fluorinated \*\*diol\*\* containing one or more aromatic or cycloaliphatic or polycyclic rings, for example those derived from the following \*\*diols\*\*: ##STR3##

## SUMMARY:

BSUM (20)

The . . . of formula I can be further polycondensed and are cross-linkable by means of the cross-linking agents usually utilized for the \*\*epoxy\*\* resins, selected from the polyfunctional compounds, in

particular from the di- and tri-functional compounds, capable of reacting with the hydroxyls and/or with the \*\*epoxy\*\* groups contained in the prepolymer.

SUMMARY:

BSUM(22)

Therefore, . . . mixed type: polyisocyanate+amine or anhydride, provided the reaction conditions are adjusted so as to allow both the reaction with the \*\*epoxy\*\* groups and the reaction with the OH groups.

SUMMARY:

BSUM(25)

There are known cross-linked fluorinated resins of the \*\*epoxy\*\* type prepared starting from epichlorohydrin, a fluorinated bisphenol and a fluorinated \*\*diol\*\* of formula:

SUMMARY:

BSUM(30)

Thus, there was the requirement to produce highly cross-linked \*\*epoxy\*\*-type resins exhibiting improved mechanical properties and offering, in particular, applicative advantages as compared with already known analogous products.

SUMMARY:

BSUM(36)

Still . . . in that it is possible to produce very thin and dimensionally stable films and furthermore, by properly choosing the comonomer \*\*diol\*\*, it is possible to achieve a high adhesion to substrates of any type. Thus, it is possible to prepare a. . .

SUMMARY:

BSUM(37)

The adhesion of these films in particular applications can be improved by using a primer, for example an \*\*epoxy\*\* primer.

SUMMARY:

BSUM(38)

The . . . higher than those exhibited by the perfluoropolyethereal blocks, such as those described in European patent application No. 212,319. Furthermore, the \*\*epoxy\*\* resins described in the abovesaid patent application exhibit a very low Tg, are particularly suitable for low-temperature applications. The polymeric. . .

SUMMARY:

BSUM(41)

A . . . fluorinated resins obtained by treating a prepolymer of general formula I with cross-linking agents which act on the hydroxy and/or \*\*epoxy\*\* groups of the starting prepolymer.

SUMMARY:

BSUM(44)

A typical example is the following: a solution-in-acetone of \*\*diol\*\* HOAOH and of \*\*diol\*\* HOR<sub>n</sub>.OH with epichlorohydrin and aqueous sodium hydroxide in excess of at least 10-20% by weight with respect to chlorine. . .

SUMMARY:

BSUM(45)

The product so obtained is a fluorinated prepolymer having values of x and y depending on the starting ratio of fluorinated \*\*diols\*\* HOAOH and HOR<sub>n</sub>.OH and on the amount of epichlorohydrin utilized. In particular, if the epichlorohydrin excess is .gtoreq.20% referred. . .

SUMMARY:

BSUM(46)

Conversely, if the utilized epichlorohydrin amount varies from 1:1 molar ratio of 20% excess with respect to the total amount of \*\*diols\*\*, the sum of indexes x and y is .gtoreq.5, and the prepolymer has prevailingly the characteristics of a polyol.

SUMMARY:

BSUM(48)

If both structural characteristics of epoxide and of polyol coexist and if only the \*\*epoxy\*\* end groups of the prepolymer are treated, resins containing functional OH groups utilizable for further subsequent reactions are obtained.

SUMMARY:

BSUM(49)

Furthermore, the viscosity of the obtained prepolymer depends on the starting ratio of \*\*diols\*\* HOAOH and HOR.<sub>n</sub>.OH to each other, and on the ratio of both to the total amount of epichlorohydrin.

SUMMARY:

BSUM(52)

The abovesaid bisepoxides are prepared by reacting epichlorohydrin with \*\*diol\*\* HOAOH or \*\*diol\*\* HOR.<sub>n</sub>.OH respectively, in the presence of NaOH in order to neutralize HCl which is formed.

SUMMARY:

BSUM(53)

By heating the bisepoxide containing radicals A or R.<sub>n</sub>.OH respectively with the \*\*diol\*\* of R.<sub>n</sub>.OH or of A and with a catalyst based on a tertiary amine (such as diazadicyclooctane and dimethylbenzylamine) at . . . y values thereof being depending on the molar ratio of the reagents containing groups A and R.<sub>n</sub>.OH. In particular, high \*\*molecular\*\* \*\*weight\*\* polymers are obtained when the epoxide/\*\*diol\*\* molar ratio is close to 1, while low \*\*molecular\*\* \*\*weight\*\* polymers are obtained when said molar ratio is close to 0.5 or to 2. The end groups will be of the \*\*epoxy\*\* or hydroxy type depending on whether an excess of bisepoxide or of \*\*diols\*\* is utilized.

SUMMARY:

BSUM(55)

For . . . polymers, i.e. block polymers and random polymers, the values of x and y can be determined by titration of the \*\*epoxy\*\* end groups or of the hydroxy groups and by NMR and IR analyses.

SUMMARY:

BSUM(56)

The cross-linkable \*\*epoxy\*\* resins of the present invention may be--depending on the fields of use--liquid, solid or in solution. The liquid \*\*epoxy\*\* resins predominantly contain \*\*epoxy\*\* groups, while the solid \*\*epoxy\*\* resins contain \*\*epoxy\*\* end groups and free hydroxy groups inside the chain. The known technology for the cross-linking of \*\*epoxy\*\* resins with conventional cross-linking agents is fully utilizable in the present invention. Thus, depending on the structure, curing can be carried out by means of the cross-linking agents commonly utilized for the \*\*epoxy\*\* resins, for example anhydrides, amines, polyamines, polyaminoamides (obtained from polyamines and dimers of fatty acids), polyphenols, polythiols, polycarboxylic acids, dipolyisocyanates, . . .

#### SUMMARY:

#### BSUM(86)

Thus, . . . two solutions having the desired viscosity, even extremely low viscosity, and containing respectively, in a proper solvent, the former the \*\*epoxy\*\* prepolymer and the latter the \*\*curing\*\* \*\*agent\*\*.

#### DETDESC:

#### DETD(2)

In . . . solvent was evaporated at 50.degree. C. under vacuum. Obtained were 290 g (yield=80%) of a fluid, transparent fluorinated prepolymer, having \*\*epoxy\*\* equivalent weight equal to 700, viscosity of 135 P at 70.degree. C. and fluorine content of 29.5%.

#### DETDESC:

#### DETD(4)

In . . . 500 cc of acetone, 156 g of fluorinated telomer [HOCH.sub.2 CH.sub.2 (CF.sub.2).sub.6 CH.sub.2 OH] (0.4 moles); 134.4 g of \*\*bisphenol\*\* \*\*AF\*\* (0.4 moles); 111 g of epichlorohydrin (1.2 moles). Separately, an aqueous solution of NaOH was prepared by dissolving 78 g. . . it was treated as described in Example 1. Obtained were 328 g (yield=82%) of a fluid, transparent fluorinated prepolymer having \*\*epoxy\*\* equivalent weight equal to 900 and fluorine content of 34%.

#### DETDESC:

#### DETD(6)

There . . . of fluorinated telomer HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (0.25 moles). In a 4-neck (1) liter flask, 100.8 g of \*\*bisphenol\*\* \*\*AF\*\* (0.3 moles) and 83.3 g of epichlorohydrin (0.9 moles) were added to the mixture obtained. Separately, an aqueous solution of . . .

DETDESC:

DETD(7)

It was then continued as described in Example 1. Obtained were 235 g of a transparent fluorinated prepolymer (yield=85%) having an \*\*epoxy\*\* equivalent weight equal to 740 and a fluorine content of 30.4%.

DETDESC:

DETD(9)

The \*\*epoxy\*\* fluorinated polymer was prepared according to Example 3 starting from a mixture of 58.5 g of fluorinated telomer HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (0.15 moles) and adding the same amounts of \*\*bisphenol\*\* \*\*AF\*\* and epichlorohydrin as are specified in example 3. Obtained were 230 g of a transparent fluorinated prepolymer having an \*\*epoxy\*\* equivalent weight equal to 800 and a fluorine content of 31.8%.

DETDESC:

DETD(11)

The fluorinated \*\*epoxy\*\* polymer was prepared in like manner as is described in Example 3 starting from a mixture of 37.5 g of . . . of 14.5 g of fluorinated telomer HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (0.05 moles) and adding the same amounts of \*\*bisphenol\*\* \*\*AF\*\* and epichlorohydrin as are indicated in Example 3. Obtained were 252 g of a transparent fluorinated prepolymer having an \*\*epoxy\*\* equivalent weight equal to 860 and a fluorine content of 33.1%.

DETDESC:

DETD(13)

Into . . . described in Example 1. Obtained were 64.5 g of a fluid fluorinated preopolymer (yield=80%), having the color of amber, an \*\*epoxy\*\* equivalent weight equal to 497 and a fluorine content of 38% by

weight.

DETDESC:

DETD(15)

Following the procedures described in Example 1, an \*\*epoxy\*\* resin was prepared by mixing 60 g of fluorinated telomer HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH (0.2 moles), 57.4 g. . . g of NaOH dissolved in 18 cc of distilled water. The resin obtained was fluid, amber-yellow, transparent and had an \*\*epoxy\*\* equivalent weight equal to 306. Thereafter, 10.52 g of this resin (0.034 \*\*epoxy\*\* equivalents) were mixed, in a 100 cc flask, with 2.88 g of \*\*bisphenol\*\* \*\*AF\*\* (0.0085 moles) and 0.1 g of diazadicyclooctane and the whole was reacted at 120.degree. C. for 10 hours. Obtained was a yellow, transparent fluorinated resin having an \*\*epoxy\*\* equivalent weight equal to 1000 and a fluorine content of 32%.

CLAIMS:

CLMS(1)

What we claim is:

1. Fluorinated \*\*epoxy\*\* resins, containing at least 10% by weight of fluorine and characterized by the structural units represented by the following formula:.. . .

20,  
B, B', equal to or different from each other, are H or ##STR12## A=a radical of a fluorinated or non-fluorinated \*\*diol\*\*, containing one or more aromatic or cycloaliphatic or polycyclic rings,  
R<sub>2</sub>.sub.f =a perfluoroalkylene radical of formula:

--(CH<sub>2</sub>).sub.q --(CF<sub>2</sub>CF<sub>2</sub>).sub.n --(CH<sub>2</sub>).sub.q --

CLAIMS:

CLMS(2)

2. The polymers according to claim 1, wherein A is derived from a \*\*diol\*\* selected from the group consisting of: ##STR14##  
=> d his

(FILE 'USPAT' ENTERED AT 11:32:55 ON 15 JUL 1997)

L1 1 S 5335004/PN  
L2 268 S BISPHENOL AF  
L3 79 S L2 AND EPOXY?  
L4 44 S L3 AND MOLECULAR WEIGHT

L5            0 S L4 AND (MOLECULAR WEIGHT (2A) EPOXY?)  
L6            13 S L4 AND (MOLECULAR WEIGHT (P) EPOXY?)  
L7            7 S L6 AND CURING AGENT  
L8            800 S (FLUORO OR FLUORINATED) (2A) ALCOHOL  
L9            225 S L8 AND EPOXY?  
L10          6 S L9 AND CURING AGENT  
L11          0 S L7 AND (LIGHT OR PHOTOLITHOGRAPHY)  
L12          0 S L7 AND UV  
L13          4 S L10 AND MOLECULAR WEIGHT  
L14          1 S L13 AND (MOLECULAR WEIGHT (P) EPOXY?)  
L15          2 S L7 AND DIOL?  
=>

• => d 183 1- cit fd

1. 5,612,167, Mar. 18, 1997, Image forming method using strippable layer and light-sensitive polymerizable layer containing silver halide; Hiroaki Yokoya, et al., 430/257, 203, 252, 253, 255, 256, 258 [IMAGE AVAILABLE]

US PAT NO: 5,612,167 [IMAGE AVAILABLE] L83: 1 of 21  
DATE FILED: Nov. 20, 1995

2. 5,599,648, Feb. 4, 1997, Surface reforming method, process for production of printing plate, printing plate and printing process; Yuji Kondo, et al., 430/256; 101/463.1, 467; 430/262, 263, 264, 291, 300, 302, 309, 327, 328, 330, 350, 353 [IMAGE AVAILABLE]

US PAT NO: 5,599,648 [IMAGE AVAILABLE] L83: 2 of 21  
DATE FILED: Nov. 26, 1993

3. 5,569,498, Oct. 29, 1996, Process for the preparation of shaped articles based on acrylic polymers coated with an antiscratch and antiabrasion film; Marco Rigamonti, et al., 427/495, 493, 519 [IMAGE AVAILABLE]

US PAT NO: 5,569,498 [IMAGE AVAILABLE] L83: 3 of 21  
DATE FILED: Jun. 6, 1995

4. 5,567,761, Oct. 22, 1996, Aqueous two-part isocyanate-free curable, polyurethane resin systems; Zhiqiang Song, 524/523; 525/127, 131, 300 [IMAGE AVAILABLE]

US PAT NO: 5,567,761 [IMAGE AVAILABLE] L83: 4 of 21  
DATE FILED: Sep. 28, 1994

5. 5,561,208, Oct. 1, 1996, Medical implement, polymer composition, and optical material; Nobukazu Takahashi, et al., 526/281; 524/81, 553; 526/280, 340, 347 [IMAGE AVAILABLE]

US PAT NO: 5,561,208 [IMAGE AVAILABLE] L83: 5 of 21  
DATE FILED: Aug. 2, 1995

6. 5,527,660, Jun. 18, 1996, Laminar imaging medium utilizing hydrophobic cycloaliphatic polyepoxide in the fracturable layers; Ganghui Teng, 430/253, 259, 273.1 [IMAGE AVAILABLE]

US PAT NO: 5,527,660 [IMAGE AVAILABLE] L83: 6 of 21  
DATE FILED: Nov. 30, 1994

7. 5,514,504, May 7, 1996, Information recording medium, and information recording a reproducing method; Masayuki Iijima, et al., 430/20; 349/89; 430/31, 48, 270.11, 495.1, 945 [IMAGE AVAILABLE]

US PAT NO: 5,514,504 [IMAGE AVAILABLE] L83: 7 of 21  
DATE FILED: Apr. 19, 1993

8. 5,468,803, Nov. 21, 1995, Medical implement, polymer composition, and optical material; Nobukazu Takahashi, et al., 524/553, 551, 570; 526/280, 281 [IMAGE AVAILABLE]

US PAT NO: 5,468,803 [IMAGE AVAILABLE] L83: 8 of 21  
DATE FILED: Mar. 1, 1993

9. 5,362,597, Nov. 8, 1994, Radiation-sensitive resin composition comprising an \*\*epoxy\*\*-containing alkali-soluble resin and a naphthoquinone diazide sulfonic acid ester; Kimiyasu Sano, et al., 430/191, 165, 192, 193, 280.1, 910 [IMAGE AVAILABLE]

US PAT NO: 5,362,597 [IMAGE AVAILABLE] L83: 9 of 21  
DATE FILED: May 27, 1992

10. 5,336,574, Aug. 9, 1994, Curable composition and process for producing shadow mask using the same; Ichiro Igarashi, et al., 430/23, 287.1, 288.1 [IMAGE AVAILABLE]

US PAT NO: 5,336,574 [IMAGE AVAILABLE] L83: 10 of 21  
DATE FILED: Oct. 2, 1992

11. 5,328,800, Jul. 12, 1994, Color image forming method using silver halide, reducing agent, polymerizable compound and colorant; Hiroaki Yokoya, et al., 430/203, 254, 255 [IMAGE AVAILABLE]

US PAT NO: 5,328,800 [IMAGE AVAILABLE] L83: 11 of 21  
DATE FILED: May 6, 1992

12. 5,326,667, Jul. 5, 1994, Image forming method and light-sensitive material using silver halide, reducing agent and polymerizable compound; Hiroaki Yokoya, et al., 430/203, 199, 202, 253, 254, 255, 257, 258, 264, 271.1, 273.1, 291 [IMAGE AVAILABLE]

US PAT NO: 5,326,667 [IMAGE AVAILABLE] L83: 12 of 21  
DATE FILED: May 6, 1992

13. 5,304,454, Apr. 19, 1994, Image forming method using silver halide, reducing agent and polymerizable compound; Hiroaki Yokoya, et al., 430/255, 253, 254, 257, 291 [IMAGE AVAILABLE]

US PAT NO: 5,304,454 [IMAGE AVAILABLE] L83: 13 of 21  
DATE FILED: May 6, 1992

14. 5,155,005, Oct. 13, 1992, Method of producing polychromatic colored image; Morimasa Sato, et al., 430/257, 7, 258 [IMAGE AVAILABLE]

US PAT NO: 5,155,005 [IMAGE AVAILABLE] L83: 14 of 21  
DATE FILED: Mar. 27, 1991

15. 5,128,391, Jul. 7, 1992, Extensible and pasteurizable radiation curable coating for metal containing organofunctional silane adhesion promoter; Paul J. Shustack, 522/92, 33, 91, 93 [IMAGE AVAILABLE]

US PAT NO: 5,128,391 [IMAGE AVAILABLE] L83: 15 of 21  
DATE FILED: Jul. 13, 1990

16. 5,128,387, Jul. 7, 1992, Extensible and pasteurizable radiation curable coating for metal; Paul J. Shustack, 522/92, 33, 91, 93 [IMAGE AVAILABLE]

US PAT NO: 5,128,387 [IMAGE AVAILABLE] L83: 16 of 21  
DATE FILED: Jul. 13, 1990

17. 5,098,766, Mar. 24, 1992, Encapsulated wire circuit board; Jeffrey D. Gelorme, et al., 428/138, 209, 415, 416, 901 [IMAGE AVAILABLE]

US PAT NO: 5,098,766 [IMAGE AVAILABLE] L83: 17 of 21  
DATE FILED: May 24, 1991

18. 5,041,470, Aug. 20, 1991, Flame retardant photocurable adhesive for wires and circuit boards; Jeffrey D. Gelorme, et al., 522/44, 79, 83, 103 [IMAGE AVAILABLE]

US PAT NO: 5,041,470 [IMAGE AVAILABLE] L83: 18 of 21  
DATE FILED: Mar. 3, 1989

19. 4,981,743, Jan. 1, 1991, Overcoat composition for optical record; Wu-Jing Ho, 428/65.1; 346/135.1; 347/264; 369/284, 288; 428/76, 694TF, 913; 430/945 [IMAGE AVAILABLE]

US PAT NO: 4,981,743 [IMAGE AVAILABLE] L83: 19 of 21  
DATE FILED: Jul. 25, 1988

20. 4,759,991, Jul. 26, 1988, Magnetic recording medium having a lubricating coating layer; Toshiyuki Kanno, et al., 428/447; 427/128, 131, 132, 502, 503; 428/522, 694TB, 694TP, 695, 900 [IMAGE AVAILABLE]

US PAT NO: 4,759,991 [IMAGE AVAILABLE]

L83: 20 of 21

DATE FILED: Mar. 1, 1985

21. 4,745,003, May 17, 1988, Method for improving durability of mirrors utilizing radiation curable coatings; Robert J. Sirkoch, et al., 427/514, 162; 522/8, 81, 89, 92, 101 [IMAGE AVAILABLE]

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(FILE 'USPAT' ENTERED AT 14:36:39 ON 15 JUL 1997)

L1 666 S 4,4-DIAMINODIPHENYLSULFONE  
L2 0 S L1 AND (CATION? (P) 4,4-DIAMINODIPHENYLSULFONE)  
L3 4 S PHENYLPHOSPHONIUM IODIDE  
L4 3 S L3 AND CATION?  
L5 0 S L4 AND (CURE OR CURING OR CURED)  
L6 0 S AROMATIC SUFONIUM SALT?  
L7 9 S SUFONIUM SALT?  
L8 0 S L7 AND L1  
L9 742 S IODONIUM SALT#  
L10 0 S L9 AND L3  
L11 6216 S CATION? POLYMER?  
L12 2085 S L11 AND (INITIATOR OR CURING AGENT)  
L13 109 S CATIONIC POLYMERIZATION INITIATOR  
L14 0 S L13 AND BISPHENOL AF  
L15 2 S L13 AND 347/CLAS  
L16 0 S L15 AND ((FLORINATED) (W) (DIOL OR GLYCOL))  
L17 0 S L12 AND ((FLORINATED) (W) (DIOL OR GLYCOL))  
L18 1224 S L12 AND (DIOL OR GLYCOL)  
L19 20 S L18 AND ((FLUORINE OR FLUORO) (P) (DIOL OR GLYCOL))  
L20 0 S L19 AND (DIPHENOL## OR POLYPHENOL##)  
L21 0 S L19 AND ((POLYHYDRIC## OR DIHYDRIC##) (W) (PHENOL##))  
L22 0 S L19 AND DIHYDROXYBENZENE  
L23 0 S L19 AND (DIPHENOL# OR POLYPHENOL#)  
L24 156 S L12 AND (DIPHENOL## OR POLYPHENOL##)  
L25 2 S L24 AND ((FLUORINE OR FLUORINATED OR FLUORO) (P) (DIPHENOL#))  
OL#  
L26 133 S L12 AND ((POLYHYDRIC OR DIHYDRIC) (W) (PHENOL##))  
L27 10 S L26 AND ((FLUORINE OR FLUORINATE? OR FLUORO) (P) (PHENOL##))  
L28 5 S L27 AND UV  
L29 0 S L28 AND ((DIOL OR GLYCOL) (P) (FLUORINE OR FLUORINATE? OR FLUORO))  
R F  
L30 5 S L28 AND (DIOL# OR GLYCOL#)  
L31 0 S L30 AND ((DIOL# OR GLYCOL#) (P) (FLUORIN? OR FLUORO))  
E CANON KABUSHIKI KAISHA/AS  
L32 15032 S E3  
L33 0 S L32 AND L19  
L34 0 S L19 AND PHOTOLITHOGRAPHY  
L35 0 S L19 AND PLASMA ETCH?  
L36 3 S L19 AND CURING AGENT  
L37 5 S L30 AND EPOXY?  
L38 10 S L19 AND EPOXY?  
L39 1 S L36 AND L38  
L40 0 S L13 AND (FLUOROPOLYOL#)

L41           17 S FLUOROPOLYOL#  
L42         1 S L41 AND CATION?  
L43         23 S FLUORINATED POLYOL#  
L44         3 S L43 AND CATION?  
L45         3 S L44 AND EPOXY?  
L46         0 S L45 AND FLUORINATED DIOL#  
L47         59 S FLUORINATED DIOL#  
L48         13 S L47 AND CATION?  
L49         3 S L48 AND EPOXY?  
L50         0 S L49 AND L45  
L51         1 S L45 AND CURING AGENT  
L52         3 S L49 AND CURING AGENT  
L53         1 S L51 AND UV  
L54         0 S L52 AND UV  
L55         0 S L52 AND PHOTOLITHOGRAPHY  
L56         3 S L52 AND (LIGHT OR PHOTON#)  
L57         0 S MONONUCLEAR FLUORINATED PHENOL  
L58         65 S MONONUCLEAR PHENOL  
L59         1 S L58 AND ((FLUORINATE? OR FLUORO) (P) (PHENOL))  
L60         0 S L59 AND EPOXY?  
L61         0 S L50 AND (EPOXY##)  
L62         0 S L59 AND CATION?  
L63         27413 S BISPHENOL  
L64         10666 S L63 AND ((EPOXY (P) BISPHENOL))  
L65         2297 S L64 AND CATION?  
L66         1792 S L65 AND CATIONIC  
L67         385 S L66 AND UV  
L68         112 S L67 AND CURING AGENT#  
L69         5 S L68 AND (DIHYDROXYBENZENE)  
L70         0 S L69 AND ((FLORINATE? OR FLUORO) (P) (DIHYDROXYBENZENE))  
L71         1 S L69 AND (FLUORINE OR FLUORO OR FLUORINATE?)  
L72         101369 S EPOXY  
L73         2706 S L72 AND FLUOROCARBON  
L74         9 S L72 AND FLUOROCARBON MOIETY  
L75         0 S L74 AND CURING AGENT  
L76         255 S L73 AND CURING AGENT  
L77         44 S L76 AND UV  
L78         7 S L77 AND (SP-170 OR SP-150 OR IRGACURE OR IODONIUM SALT##  
OR  
L79         1504 S (FC-430 OR FLUORAD)  
L80         662 S L79 AND EPOXY  
L81         295 S L80 AND HYDROXYL#  
L82         37 S L81 AND (SP-170 OR SP-150 OR IRGACURE)  
L83         21 S L82 AND (FLUORO OR FLUORINE OR FLUORINATE?)

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